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Single Liquid Source Plasma Enhanced Metalorganic Chemical Vapor Deposition of $YBa_2Cu_3O_{7-x}$ Thin Films

by

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SINGLE LIQUID SOURCE PLASMA ENHANCED METALORGANIC CHEMICAL VAPOR DEPOSITION OF HIGH-QUALITY $YBa_2Cu_3O_{7-x}$ THIN FILMS

Jiming Zhang, Robin A. Gardiner, Peter S. Kirlin, Robert W. Boerstler, and John Steinbeck, Advanced Technology Materials, Inc., Danbury, CT 06810

ABSTRACT

High quality $YBa_2Cu_3O_{7-x}$ films were grown *in-situ* on $LaAlO_3$ (100) by a novel single liquid source plasma-enhanced metalorganic chemical vapor deposition process. The metalorganic complexes $M(thd)_n$, (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate; M = Y, Ba, Cu) were dissolved in an organic solution and injected into a vaporizer immediately upstream of the reactor inlet. The single liquid source technique dramatically simplifies current CVD processing and can significantly improve the process reproducibility. X-ray diffraction measurements indicated that single phase, highly c-axis oriented $YBa_2Cu_3O_{7-x}$ was formed *in-situ* at a substrate temperature 680 °C. The as-deposited films exhibited a mirror-like surface, had transition temperature $T_{c0} \cong 89$ K, $\Delta T_c < 1$ K, and $J_c(77K) = 10^6$ A/cm^2.

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Metalorganic chemical vapor deposition (MOCVD) has been shown to be a promising technique for the fabrication of device quality compound semiconductors and high-T_c superconducting thin films.[1-6] Using MOCVD, films of the important classes of high-T_c superconductors have been deposited and shown to have properties comparable to thin films prepared by physical vapor deposition (PVD) techniques.[2-6] In principle, CVD offers the advantages of high throughput, the capability of coating complex shapes, low equipment costs, and ease of scale-up to manufacturing volumes. However, the routine preparation of high-quality superconducting thin films by MOCVD has been impeded by the difficulties of reproducibly transporting the metalorganic precursors to the substrate.[7] Standard delivery systems (bubblers) require the control of the temperature and flow rate for each precursor. The metalorganic precursors (especially the Ba precursor) currently used in the CVD preparation of high-T_c superconductors are not stable at the requisite sublimation temperatures, making accurate control of the film stoichiometry difficult over time.[7] In this communication, we report a novel single liquid source MOCVD technique to prepare superconducting $YBa_2Cu_3O_{7-x}$ thin films. The single liquid source technique dramatically simplifies current CVD processing and can significantly improve the process reproducibility. The methodology reported here differs significantly from two other recently reported single source approaches.[8,9]

$YBa_2Cu_3O_{7-x}$ films were grown in an inverted vertical reactor specially configured for the growth of complex oxides (Fig. 1). A rf plasma (f = 13.56 MHz, P = 100 W) was introduced to the deposition region in a down stream (remote) configuration. In this configuration, the plasma is generated far from the substrate and activated species are introduced into the deposition region through a quartz tube. The remote plasma configuration was selected to avoid pre-deposition gas phase reactions and ion bombardment of the surface of the films.[10] A mixture of O_2 (flow rate = 500 sccm) and N_2O (flow rate = 250 sccm) was used as

the reactant gas. The total pressure of the reactor was 1.5 torr. The $LaAlO_3$ (100) substrates were held on a SiC susceptor which was heated by quartz-halogen lamps from the back surface. The substrate temperature was measured by a fine thermocouple in direct contact with the surface of the substrate.

The ß-diketonate complexes $Y(thd)_3$, $Ba(thd)_2$ and $Cu(thd)_2$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate) were dissolved in a mixture of tetrahydrofuran (THF), isopropanol (IPA) and tetraglyme in a ratio of 8:2:1. The molarity of the solution was 0.40 mol/l. The film composition was controlled by varying the molar ratio of the complexes in the solution. The Y:Ba:Cu molar ratio in the solution was 1:4:4. THF was chosen as a solvent because of its large solubility and compatibility with the precursors. IPA and tetraglyme were added to lower the evaporation rate of the solution and increase the stability of $Ba(thd)_2$ during evaporation. The solution was injected by a liquid pump into a heated, stainless steel vaporizer which was maintained at 230 °C during the deposition (Fig. 1). The transport rate of the solution to the vaporizer was 3 -6 mm^3/min. The precursor vapor was carried upstream of the reactor inlet by nitrogen carrier gas (flow rate = 50 sccm) and the vaporization process takes place on a continuous basis. The deposition rates were 0.2 - 0.5 μm/hr and the typical film thickness was 0.3 -0.5 μm, although continuous films as thin as 0.1 μm have been deposited.

To complete $YBa_2Cu_3O_{7-x}$ film oxidation, the deposition chamber was backfilled to ~ 100 Torr with oxygen gas while the substrates were slowly cooled to room temperature at a rate 10 °C /min. The composition of the films was measured by energy dispersive X-ray analysis (EDX). The standard deviations of the Y, Cu, and Ba atomic ratios determined by the EDX analysis were 1.6, 3.7, and 4.4 percent, respectively, indicating the single liquid source technique yields reproducible results. The deposition reproducibility is achieved because the source reagents in the single liquid source technique are at their vaporization

temperature for a very short time rather than the entire time of the deposition run; consequently the partial pressure of all the source reagents remain constant during growth. High quality superconducting films were found to be consistently Ba deficient and Cu rich which is consistent with a recent report by Zhao et al.[11]

The microstructure of the films was characterized by XRD using Ni-filtered Cu $K\alpha$ radiation. Fig. 2 shows the X-ray diffraction pattern for a typical $YBa_2Cu_3O_{7-x}$ film deposited at 680 °C by PE-MOCVD. As can be seen from the figure, single phase, highly c-axis oriented $YBa_2Cu_3O_{7-x}$ was formed by single liquid source PE-MOCVD. The c-axis repeat distance derived from the (00l) x-ray peaks is 11.68-11.69 Å, corresponding to $YBa_2Cu_3O_{7-x}$ with nearly complete oxidation ($x < 0.1$).[12] Rocking curves obtained from the $YBa_2Cu_3O_{7-x}$ (005) reflection displayed a full width at half maximum as low as 0.32°. The as-deposited films were smooth and exhibited a mirror-like surface. Scanning electron micrographs of two $YBa_2Cu_3O_{7-x}$ films, one 0.1 μm thick (Fig. 3a), and another 0.4 μm thick (Fig. 3b) both indicated the formation of continuous dense material. The particulates scattered on the film surface are typical of $YBa_2Cu_3O_{7-x}$ films grown by MOCVD.[13,14] It is noteworthy that there are significantly more particulates scattered on the surface of 0.4 μm thick film than the 0.1 μm thick film. Similar observations have also been made recently by DeSisto et al for their $YBa_2Cu_3O_{7-x}$ films prepared by MOCVD.[14]

The superconducting properties of our $YBa_2Cu_3O_{7-x}$ films were characterized by both inductive and four point probe resistivity measurements. Fig. 4 shows the relative inductance change of an *in-situ* $YBa_2Cu_3O_{7-x}$ film measured using a Lakeshore screening system. The sharp transition in the inductance data indicates that the film is nearly single phase $YBa_2Cu_3O_{7-x}$ with a $T_c = 89.5$ K and $\Delta T_c = 0.4$ K. The electrical resistivity ρ was measured using a four point probe technique. Typical $\rho(T)$ results show that ρ decreases nearly

linearly with T until the film enters the superconducting state at $T_{c0} = 89$ K. Measurements of the critical current density J_c were carried out by both dc susceptibility[15] and transport tecchniques. Susceptibility measurements show that the J_c (77 K) = 10^6 A/cm^2. Transport measurements of J_c were carried out using a 1.2 cm long, 10 μm wide transmission line. These measurements yield a J_c (77 K) = 3.3 x 10^5 A/cm^2 using the 1 μV/cm criterion.

In summary, our results show that high-quality superconducting $YBa_2Cu_3O_{7-x}$ were prepared *in-situ* on (100) $LaAlO_3$ by a novel single liquid source plasma-enhanced metalorganic chemical vapor deposition process at a substrate temperature of 680 °C. The single liquid source process dramatically simplifies current CVD processing and can significantly improve the process reproducibility. Both four probe resistivity and inductive measurements revealed that the as-deposited $YBa_2Cu_3O_{7-x}$ films have superconducting transition temperature $T_{c0} \cong 89$ K and $\Delta T_c < 1$ K. Critical current densities J_c at 77 K derived from magnetic measurement was 10^6 A/cm^2. A 1.2 cm long, 10 μm wide $YBa_2Cu_3O_{7-x}$ tansmission line yielded a $J_c = 3.3 \times 10^5$ A/cm^2 at 77 K.

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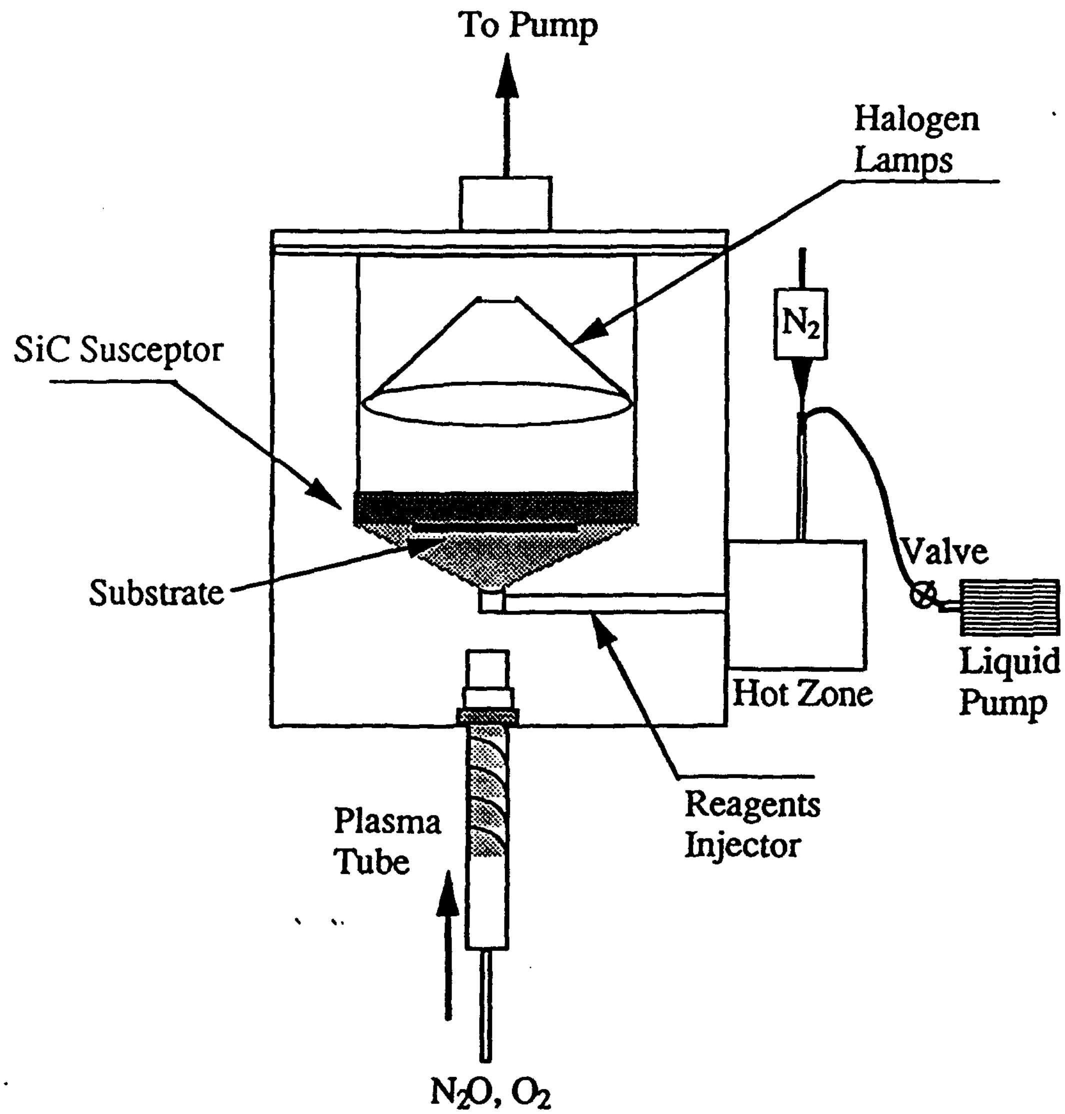
Figure captions:

Fig. 1 Schematic diagram of single liquid source CVD reactor.

Fig. 2 X-ray diffraction pattern for a typical $YBa_2Cu_3O_{7-x}$ film on $LaAlO_3$ (100) substrate by single liquid source PE-MOCVD.

Fig. 3 Scanning Electron Micrographs of $YBa_2Cu_3O_{7-x}$ films on $LaAlO_3$ (100) substrate by single liquid source PE-MOCVD; (a) 0.1 μm thick. (b) 0.4 μm thick.

Fig. 4 Inductive measurement data for a typical $YBa_2Cu_3O_{7-x}$ film on $LaAlO_3$ (100) substrate by single liquid source PE-MOCVD.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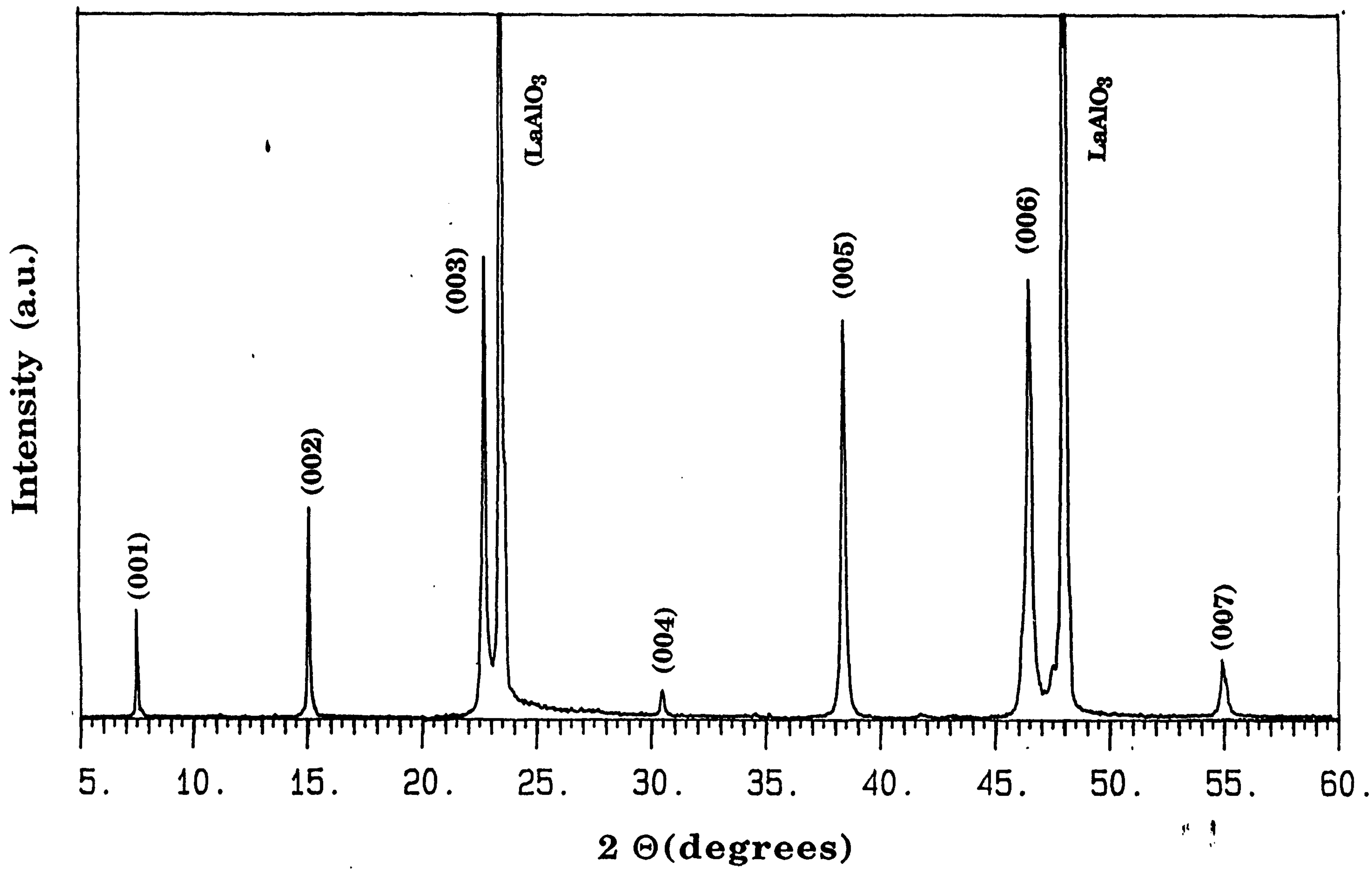
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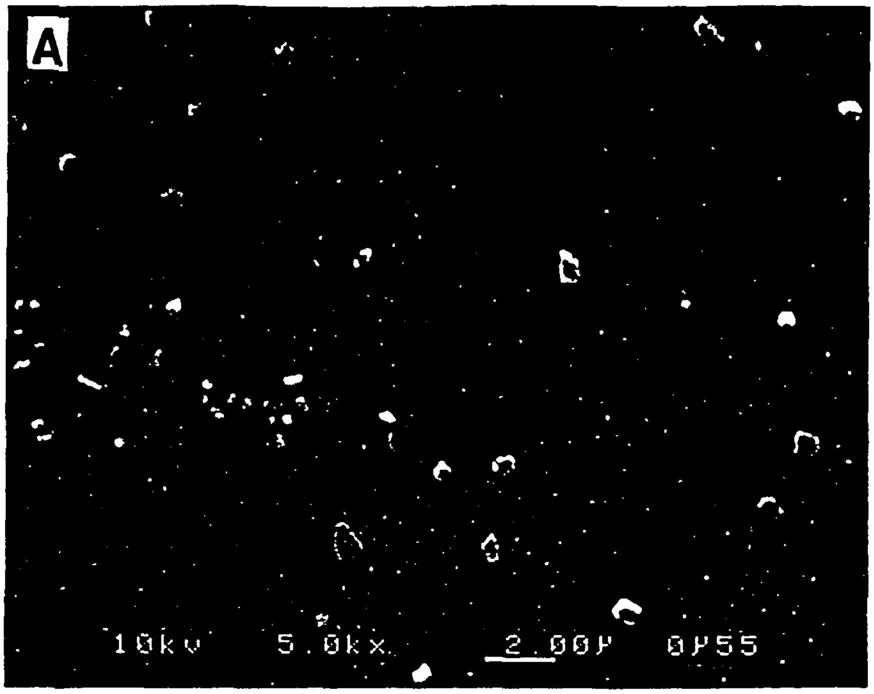
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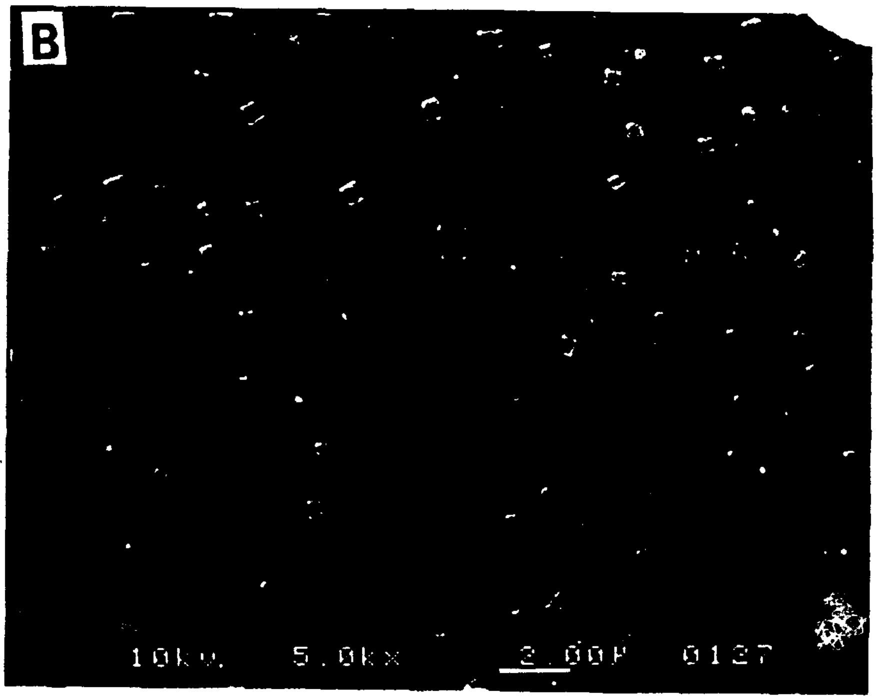
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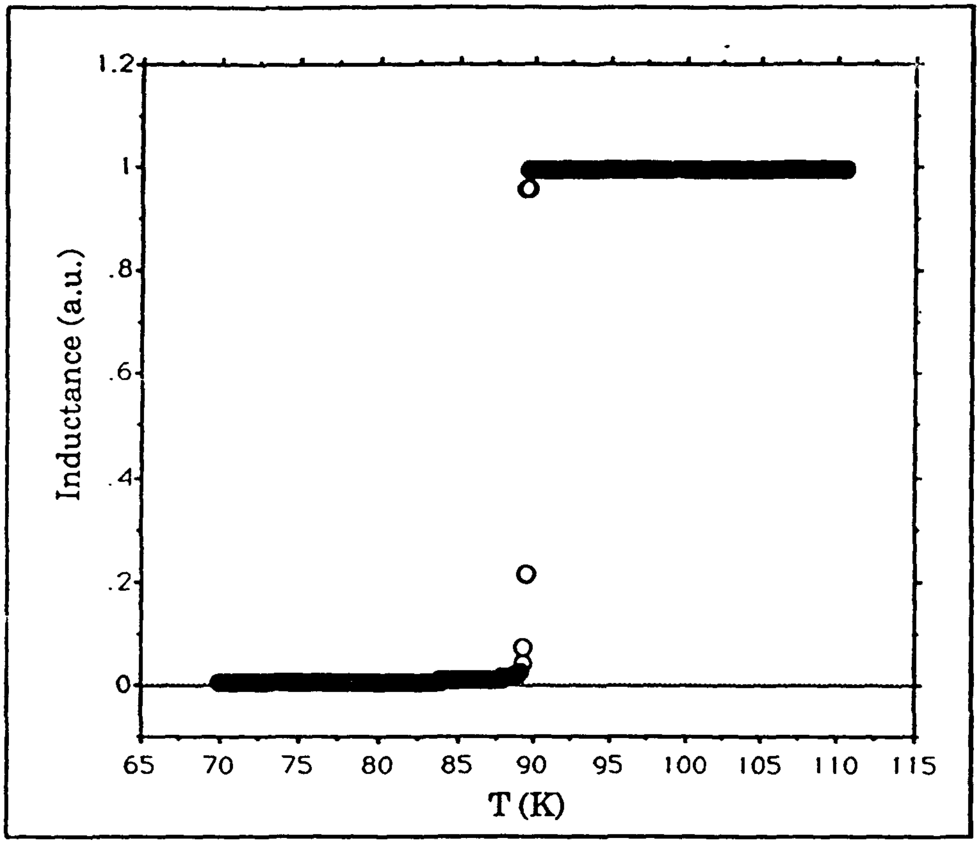
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